

Wigner's phase space function and atomic structure

I. The hydrogen atom ground state

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(Received 25 May 1982 ; accepted 29 June 1982)

We have constructed the Wigner function for the ground state of the hydrogen atom and analysed its variation over phase space. By means of the Weyl correspondence between operators and phase space functions we have then studied the description of angular momentum and resolved a dilemma in the comparison with early quantum mechanics. Finally we have discussed the introduction of local energy densities in coordinate space and demonstrated the validity of a local virial theorem.

1. INTRODUCTION

This is the first of a series of papers devoted to the phase space description of atomic and molecular systems. Phase space representations of quantum mechanics have been extensively discussed since the classical works by Weyl [1], Wigner [2], Groenewold [3] and Moyal [4]. They have been applied in quantum statistical studies of transport processes and radiation (see, for example, [5] and [6]), and in treatments of molecular and nuclear dynamics (for example, [7-10]). They have, however, not yet been used in such detailed theories as the theories of atomic and molecular electronic structure.

In this and forthcoming papers we shall investigate the possibility of extending the application of phase space representations to such theories as well. Very accurate wavefunctions are now available for all atoms and for a large class of molecules. These wavefunctions have always been generated in coordinate space, but there has been a considerable interest in their momentum space representatives as well. The use of phase space representations allows one to include the coordinate and momentum characteristics in a single picture, and hence it may serve to improve our understanding of the dynamical behaviour of electrons in atoms and molecules.

The phase space formulation of quantum mechanics treats states and transitions in an equivalent manner. Thus, there is a phase space function associated with every quantum state and with every quantum transition as well. This function is the Wigner function.

In the present paper we shall only consider Wigner functions associated with states. Operationally, such functions play the rôle of probability densities in phase space. The values of the functions are, however, not restricted to being positive or zero, although they are always real. Hence, one may not *interpret* the functions as probability densities. Such an interpretation would of course also be inconsistent with the uncertainty principle.

If a Wigner function cannot be interpreted as a probability density, how may it then be interpreted? This question, which has attracted considerable attention, was discussed in a recent article by one of the authors [11]. The conclusion is that one must reconsider the rôle played by a point in phase space. The significance of such a point is not, as in classical mechanics, that it defines a simultaneous position and momentum of a particle. It is instead that it defines an inversion operator, the so-called Wigner operator [12, 13].

The properties of the Wigner operator and the group theoretical basis it lends to the phase space representation of quantum mechanics has been thoroughly discussed by one of us [14], but since only one-dimensional motion was considered we shall here list a few of the relevant expressions for a particle in three dimensions.

The inversion operator defined by the phase space point (\mathbf{r}, \mathbf{p}) is

$$\hat{\Pi}(\mathbf{r}, \mathbf{p}) = \left(\frac{1}{2\hbar}\right)^3 \int \int d\mathbf{u} d\mathbf{v} \exp \left[\frac{i}{\hbar} (\mathbf{r} \cdot \mathbf{u} + \mathbf{p} \cdot \mathbf{v}) \right] \times \exp \left[-\frac{i}{\hbar} (\hat{\mathbf{r}} \cdot \mathbf{u} + \hat{\mathbf{p}} \cdot \mathbf{v}) \right] \quad (1)$$

with the caret (^) denoting operators. The Wigner function associated with a normalized state vector $|\psi\rangle$ is

$$f(\mathbf{r}, \mathbf{p}) = \left(\frac{2}{\hbar}\right)^3 \langle \psi | \hat{\Pi}(\mathbf{r}, \mathbf{p}) | \psi \rangle. \quad (2)$$

It is normalized such that

$$\int \int f(\mathbf{r}, \mathbf{p}) d\mathbf{r} d\mathbf{p} = 1. \quad (3)$$

If $\psi(\mathbf{r})$ and $\phi(\mathbf{p})$ are the coordinate and momentum wavefunctions, respectively, that is

$$\psi(\mathbf{r}) = \langle \mathbf{r} | \psi \rangle, \quad (4)$$

$$\phi(\mathbf{p}) = \langle \mathbf{p} | \psi \rangle, \quad (5)$$

then we may also write

$$f(\mathbf{r}, \mathbf{p}) = \left(\frac{2}{\hbar}\right)^3 \int d\mathbf{r}' \psi(\mathbf{r}-\mathbf{r}')^* \psi(\mathbf{r}+\mathbf{r}') \exp \left(-\frac{2i}{\hbar} \mathbf{p} \cdot \mathbf{r}' \right) \quad (6)$$

and

$$f(\mathbf{r}, \mathbf{p}) = \left(\frac{2}{\hbar}\right)^3 \int d\mathbf{p}' \phi(\mathbf{p}-\mathbf{p}')^* \phi(\mathbf{p}+\mathbf{p}') \exp \left(\frac{2i}{\hbar} \mathbf{r} \cdot \mathbf{p}' \right). \quad (7)$$

Further we have the relations

$$\int d\mathbf{p} f(\mathbf{r}, \mathbf{p}) = \psi(\mathbf{r})^* \psi(\mathbf{r}), \quad (8)$$

$$\int d\mathbf{r} f(\mathbf{r}, \mathbf{p}) = \phi(\mathbf{p})^* \phi(\mathbf{p}), \quad (9)$$

and

$$\langle \psi | \hat{a} | \psi \rangle = \int \int d\mathbf{r} d\mathbf{p} f(\mathbf{r}, \mathbf{p}) a(\mathbf{r}, \mathbf{p}), \quad (10)$$

where $a(\mathbf{r}, \mathbf{p})$ is the Weyl transform [1] of the operator \hat{a} , as discussed in the Appendix.

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It is the relations (3) and (8)–(10) that show how the Wigner function plays the rôle of a probability density in an operational sense. Let us also note that the eigenvalues of $\hat{\Pi}(\mathbf{r}, \mathbf{p})$ must be ± 1 , since it is an inversion operator. Hence [13] we get that

$$|f(\mathbf{r}, \mathbf{p})| \leq \left(\frac{2}{h}\right)^3 \quad (11)$$

and consequently that $f(\mathbf{r}, \mathbf{p})$ must have support in a volume not smaller than $(h/2)^3$.

With the value of f at the point (\mathbf{r}, \mathbf{p}) being equal to $2/h$ times the overlap between $1\psi\rangle$ and its mirror image with respect to (\mathbf{r}, \mathbf{p}) , we may say that $f(\mathbf{r}, \mathbf{p})$ is a measure of the way the point (\mathbf{r}, \mathbf{p}) supports the given quantum state. Similarly, we may talk about the way a certain region or a certain trajectory in phase space supports a state. A proper use of this kind of language leads to an integrated description of the wave and particle characteristics of quantum states.

It is the purpose of the present paper to show how this kind of description works for the ground state of the hydrogen atom.

2. THE WIGNER FUNCTION FOR $1s$ ORBITALS

In what follows we shall use atomic units, and hence put m , e and \hbar equal to one, m being the electron's mass and $-e$ its charge. We shall consider nuclear masses as infinite and exclude spin and relativistic effects. The hamiltonian for a hydrogen-like atom with nuclear charge Z is then

$$H = \frac{\hat{p}^2}{2} - \frac{Z}{\hat{r}}. \quad (12)$$

The coordinate wavefunction for the ground state has the well known form

$$\psi_{1s}(\mathbf{r}) = \left(\frac{Z^3}{\pi}\right)^{1/2} \exp(-Zr) \quad (13)$$

and the corresponding momentum wavefunction is [15]

$$\phi_{1s}(\mathbf{p}) = \frac{2\sqrt{2}}{\pi} Z^{5/2} \frac{1}{(p^2 + Z^2)^2}. \quad (14)$$

Thus we obtain the following equivalent expressions for the Wigner function by using equations (6) and (7)

$$f_{1s}(\mathbf{r}, \mathbf{p}) = \frac{Z^3}{\pi^4} \int d\mathbf{r}' \exp(-Z|\mathbf{r} - \mathbf{r}'|) \exp(-Z|\mathbf{r} + \mathbf{r}'|) \exp(-2i\mathbf{p} \cdot \mathbf{r}') \quad (15)$$

and

$$f_{1s}(\mathbf{r}, \mathbf{p}) = \frac{8Z^5}{\pi^5} \int d\mathbf{p}' [(\mathbf{p} - \mathbf{p}')^2 + Z^2]^{-2} [(\mathbf{p} + \mathbf{p}')^2 + Z^2]^{-2} \exp(2i\mathbf{r} \cdot \mathbf{p}'). \quad (16)$$

Neither of the integrals involved can be evaluated in a closed analytical form and the Wigner function is consequently not expressible in terms of standard functions. This is in accordance with the fact that it satisfies a differential equation of infinitely high order [16], while the usual standard functions satisfy differential equations of the first or second order.

The integrals (15) and (16) are, however, not newcomers in the theory of electronic structures. The integral (15) is, for a fixed value of \mathbf{r} , the Fourier transform of the product of two $1s$ orbitals centred around the points $-\mathbf{r}$ and \mathbf{r} respectively. Thus it is recognized as a generalized scattering factor in the theory of X-ray diffraction of molecular crystals and as a standard integral in those band theories of solids that are based on Fourier transform methods. Several procedures have, accordingly, been devised for the evaluation of this integral by methods of approximation.

Thus, McWeeny [17] and Silverstone [18] have studied methods in which one orbital is expanded in an infinite series about the origin of the other. Such methods are only rapidly convergent for small values of \mathbf{r} , and hence they are not applicable in the present context where all values of \mathbf{r} must be considered. Other methods implying the summation of an infinite series or the numerical evaluation of an integral have been suggested by several authors ([19–21] and references therein). Although very powerful for single values of \mathbf{r} where the accuracy can be readily assessed, these methods are again not easily applied when \mathbf{r} is allowed to vary freely.

The natural procedure to follow in the present context is to approximate the function (13) by a finite series of gaussians and insert this series in (15). The resulting integrals can then be evaluated analytically. This method is capable of giving a good representation of the Wigner function for all values of \mathbf{r} and \mathbf{p} , and it can easily be extended to other orbitals than the $1s$ orbital. Generalized scattering factors have been calculated along these lines by McWeeny [22] and Stewart [23].

We write accordingly

$$\psi_{1s}^{(M)}(\mathbf{r}) = \sum_{i=1}^M c_i \chi_i(\mathbf{r}) \quad (17)$$

with $\chi_i(\mathbf{r})$ being a normalized gaussian

$$\chi_i(\mathbf{r}) = \left(\frac{2\alpha_i}{\pi}\right)^{3/4} \exp(-\alpha_i r^2). \quad (18)$$

This gives

$$f_{1s}^{(M)}(\mathbf{r}, \mathbf{p}) = \sum_{i=1}^M c_i^2 P_{ii}(\mathbf{r}, \mathbf{p}) + \sum_{i>j=1}^M c_i c_j \{P_{ij}(\mathbf{r}, \mathbf{p}) + P_{ji}(\mathbf{r}, \mathbf{p})\} \quad (19)$$

where we have used the definition

$$P_{ij}(\mathbf{r}, \mathbf{p}) = \frac{1}{\pi^3} \int d\mathbf{r}' \chi_i(\mathbf{r} - \mathbf{r}') \chi_j(\mathbf{r} + \mathbf{r}') \exp(-2i\mathbf{p} \cdot \mathbf{r}'). \quad (20)$$

A straightforward integration results in

$$P_{ij}(\mathbf{r}, \mathbf{p}) = \frac{1}{\pi^3} \left(\frac{\gamma_{ij}}{\alpha_i + \alpha_j}\right)^{3/4} \exp(-\gamma_{ij} r^2) \exp\left(-\frac{p^2}{\alpha_i + \alpha_j}\right) \exp(2i\tau_{ij}\mathbf{p} \cdot \mathbf{r}) \quad (21)$$

in which

$$\gamma_{ij} = \frac{4\alpha_i\alpha_j}{\alpha_i + \alpha_j} \quad (22)$$

and

$$\tau_{ij} = \frac{\alpha_i - \alpha_j}{\alpha_i + \alpha_j}. \quad (23)$$

Hence we get

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$$f_{1s}^{(M)}(\mathbf{r}, \mathbf{p}) = \frac{1}{\pi^3} \sum_{i=1}^M c_i^2 \exp(-2\alpha_i r^2) \exp\left(-\frac{p^2}{2\alpha_i}\right) + \frac{2}{\pi^3} \sum_{i>j=1}^M c_i c_j \left(\frac{\gamma_{ij}}{\alpha_i + \alpha_j}\right)^{3/4} \\ \times \exp(-\gamma_{ij} r^2) \exp\left(-\frac{p^2}{\alpha_i + \alpha_j}\right) \cos(2\tau_{ij} \mathbf{p} \cdot \mathbf{r}). \quad (24)$$

In the following sections we shall study this expression for the hydrogen atom, using an $M=10$ representation of the $1s$ orbital determined by Duijneveldt [24]. This is the extremely good approximation to the true $1s$ orbital, leading for instance to an energy which only deviates 0.00015 per cent from the true value. The parameters defining the expansion are reproduced in table 1.

Table 1. Gaussian approximation to the $1s$ hydrogen orbital [24].

i	α_i/a_0^{-2}	c_i
1	0.062157	0.107330
2	0.138046	0.339658
3	0.304802	0.352349
4	0.710716	0.213239
5	1.794924	0.090342
6	4.915078	0.030540
7	15.018344	0.008863
8	54.698039	0.002094
9	254.017712	0.000372
10	1776.775559	0.000044

We shall also make certain comparisons with the variationally determined $M=1$ representation of the hydrogen $1s$ orbital. As is well known, this approximation is obtained for $\alpha = 8/9\pi = 0.282942 a_0^{-2}$.

3. A CHANGE OF VARIABLES

The Wigner function is a function in six-dimensional phase space. It is, however, obvious from (24) that $f_{1s}(\mathbf{r}, \mathbf{p})$ only depends upon the three quantities r , p and u , with u being the angle between the vectors \mathbf{r} and \mathbf{p} . Let us therefore define new phase space variables instead of

$$\mathbf{r} = (x_1, x_2, x_3) \quad (25)$$

and

$$\mathbf{p} = (p_1, p_2, p_3) \quad (26)$$

by introducing three mutually orthogonal unit vectors [25]

$$\left. \begin{aligned} \mathbf{e}_1 &= \frac{1}{2 \sin u/2} \left(\frac{\mathbf{r}}{r} - \frac{\mathbf{p}}{p} \right), \\ \mathbf{e}_2 &= \frac{1}{2 \cos u/2} \left(\frac{\mathbf{r}}{r} + \frac{\mathbf{p}}{p} \right), \\ \mathbf{e}_3 &= \frac{1}{rp \sin u} \mathbf{r} \times \mathbf{p} = \mathbf{e}_1 \times \mathbf{e}_2. \end{aligned} \right\} \quad (27)$$

These vectors define a right handed coordinate system S in ordinary three-space. The orientation of S with respect to a laboratory system S_0 may be specified by three Euler angles α, β, γ such that S is obtained from S_0 by

- (1) a rotation about the third axis of S_0 through the angle α ,
- (2) a rotation about the new second axis through the angle β ,
- (3) a rotation about the new third axis through the angle γ .

The following relations are then valid :

$$\left. \begin{aligned} x_1 &= -r \left[\cos \alpha \cos \beta \sin \left(\gamma - \frac{u}{2} \right) + \sin \alpha \cos \left(\gamma - \frac{u}{2} \right) \right] \\ x_2 &= -r \left[\sin \alpha \cos \beta \sin \left(\gamma - \frac{u}{2} \right) - \cos \alpha \cos \left(\gamma - \frac{u}{2} \right) \right] \\ x_3 &= r \sin \beta \sin \left(\gamma - \frac{u}{2} \right) \end{aligned} \right\} \quad (28)$$

$$\left. \begin{aligned} p_1 &= -p \left[\cos \alpha \cos \beta \sin \left(\gamma + \frac{u}{2} \right) + \sin \alpha \cos \left(\gamma + \frac{u}{2} \right) \right] \\ p_2 &= -p \left[\sin \alpha \cos \beta \sin \left(\gamma + \frac{u}{2} \right) - \cos \alpha \cos \left(\gamma + \frac{u}{2} \right) \right] \\ p_3 &= p \sin \beta \sin \left(\gamma + \frac{u}{2} \right) \end{aligned} \right\} \quad (29)$$

and

$$dr dp = r^2 dr p^2 dp \sin u du \sin \beta d\beta d\alpha d\gamma. \quad (30)$$

The quantities $r, p, u, \alpha, \beta, \gamma$ are our new phase space variables; r and p range from 0 to ∞ , u and β from 0 to π , α and γ from 0 to 2π .

We shall refer to the plane defined by \mathbf{r} and \mathbf{p} as the dynamical plane. Its normal, which is \mathbf{e}_3 , has the spherical polar coordinates (β, α) . The angle γ will be called the dynamical angle.

With these designations we may express the fact that f_{1s} is independent of α, β and γ by saying, that all dynamical planes and all dynamical angles are equivalent. By displaying the dependence on r, p and u we obtain a complete picture of the $1s$ -state in the phase space representation. Let us first consider the picture obtained in the $M=1$ approximation.

4. THE SINGLE GAUSSIAN APPROXIMATION TO THE $1s$ STATE

This simple approximation corresponds to a coordinate wavefunction of the form (18), that is

$$\psi_{1s}^{(1)}(\mathbf{r}) = \left(\frac{2\alpha}{\pi} \right)^{3/4} \exp(-\alpha r^2) \quad (31)$$

with $\alpha = 8/9\pi = 0.282942 a_0^{-2}$. The corresponding momentum wavefunction is

$$\phi_{1s}^{(1)}(\mathbf{p}) = \left(\frac{1}{2\pi\alpha} \right)^{3/4} \exp\left(-\frac{p^2}{4\alpha}\right) \quad (32)$$

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Figure 1. Contour value, 0.6 the maximum

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and the Wigner function (24) becomes

$$f_{1s}^{(1)}(\mathbf{r}, \mathbf{p}) = \frac{1}{\pi^3} \exp(-2\alpha r^2) \exp\left(-\frac{p^2}{2\alpha}\right). \quad (33)$$

This function is not only independent of α , β and γ . It is independent of u as well. By integrating it over α , β , γ , u and multiplying it with $r^2 p^2$ we obtain the function

$$F_{1s}^{(1)}(r, p) = \frac{16}{\pi} r^2 p^2 \exp(-2\alpha r^2) \exp\left(-\frac{p^2}{2\alpha}\right) \quad (34)$$

which is normalized such that

$$\int_0^\infty \int_0^\infty F_{1s}^{(1)}(r, p) dr dp = 1. \quad (35)$$

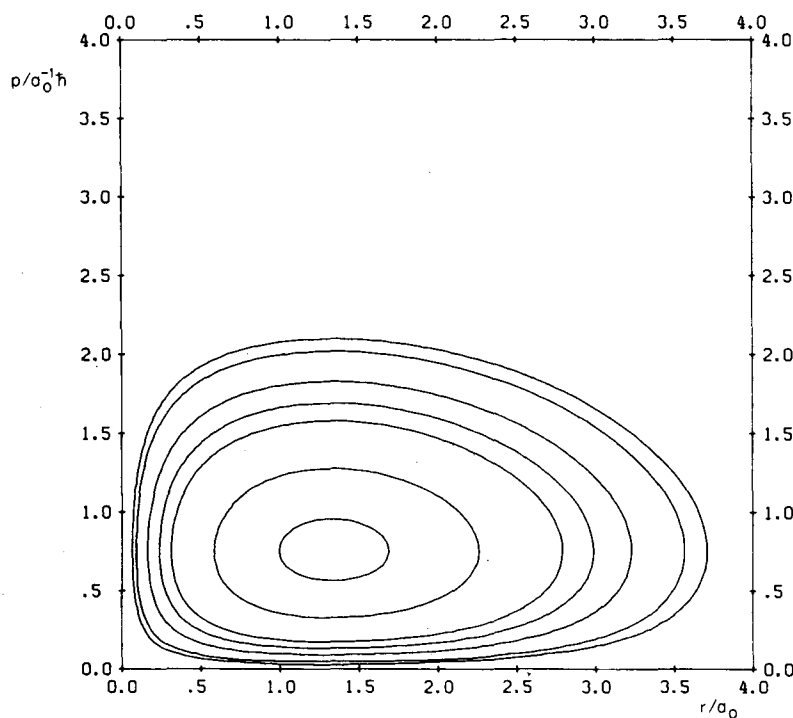


Figure 1. Contour map of the function $F_{1s}^{(1)}(r, p)$. The function attains its maximum value, $0.6893 \hbar^{-1}$, at the point $(r_0, p_0) = (1.3293 a_0, 0.7523 a_0^{-1} \hbar)$. Starting from the maximum, contours have been drawn at $0.6, 0.3, 0.1, 0.06, 0.03, 0.01, 0.006 \hbar^{-1}$.

The function $F_{1s}^{(1)}(r, p)$ is displayed in figure 1 through a contour map. As is evident from (34) it is everywhere non-negative. It has a maximum at the point

$$(r_0, p_0) = \left(\frac{1}{\sqrt{(2\alpha)}}, \sqrt{(2\alpha)} \right) = (1.3293 a_0, 0.7523 a_0^{-1} \hbar) \quad (36)$$

the maximum value being

$$F_{1s}^{(1)}(r_0, p_0) = \frac{16}{\pi e^2} = 0.6893 \hbar^{-1}. \quad (37)$$

It is obvious that $F_{1s}^{(1)}(r, p)$ gives us complete information about the 1s state in the single gaussian approximation. Thus, integration over p gives the radial density in configuration space (with maximum at r_0) and integration over r gives the radial density in momentum space (with maximum at p_0). Actually $F_{1s}^{(1)}$ is nothing but the product of these two radial densities.

As far as the function $f_{1s}^{(1)}(r, p)$ itself is concerned, we note that it attains its maximum at the origin $(0, 0)$. The 1s state is symmetric with respect to inversion in this point, and the corresponding value of $f_{1s}^{(1)}$ is accordingly the largest possible one, which from the relation (11) is known to be $(2/h)^3$, that is, $(1/\pi)^3 \hbar^{-3}$ in atomic units.

5. THE $M=10$ DESCRIPTION OF THE 1s STATE

This description, whose parameters are listed in table 1, is as previously mentioned an exceedingly accurate one. The Wigner function, for which we have the expression (24), is no longer independent of u and hence we cannot display all its features by means of a single contour map of the type shown in figure 1. A complete picture requires the drawing of a map for each value of u in the interval $0 \leq u \leq \pi/2$. As is obvious from the expression (24), we obtain the same maps for u and $\pi - u$.

It is still expedient to integrate the expression (24) over α, β and γ and to multiply with $r^2 p^2$. Hence we obtain the function

$$F_{1s}(r, p, u) = 8\pi^2 r^2 p^2 f_{1s}^{(10)}(r, p). \quad (38)$$

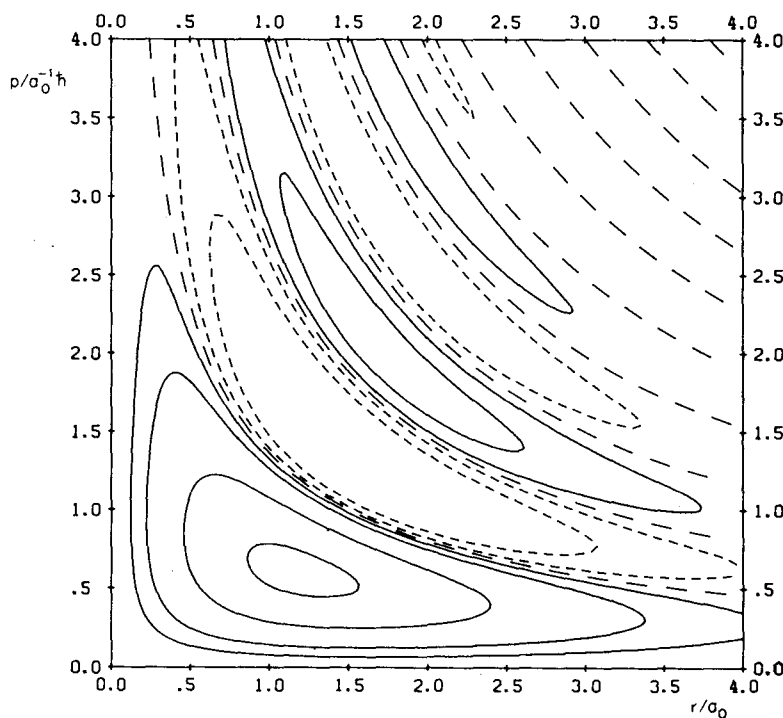


Figure 2. Contour map of the function $F_{1s}(r, p, u)$ for $u=0$. Starting from the nodal curves (dashed lines, contour value (0.0)) contours have been drawn at $0.01, 0.03, 0.1, 0.2 \hbar^{-1}$ (solid lines), $-0.01, -0.03 \hbar^{-1}$ (dotted lines).

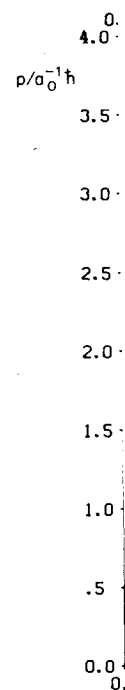


Figure 4. Contour map of the function $F_{1s}(r, p, u)$ for $u=0$. Starting from the nodal curves (dashed lines, contour value (0.0)) contours have been drawn at $0.06, 0.03, 0.01 \hbar^{-1}$ (solid lines), $-0.06, -0.03, -0.01 \hbar^{-1}$ (dotted lines).

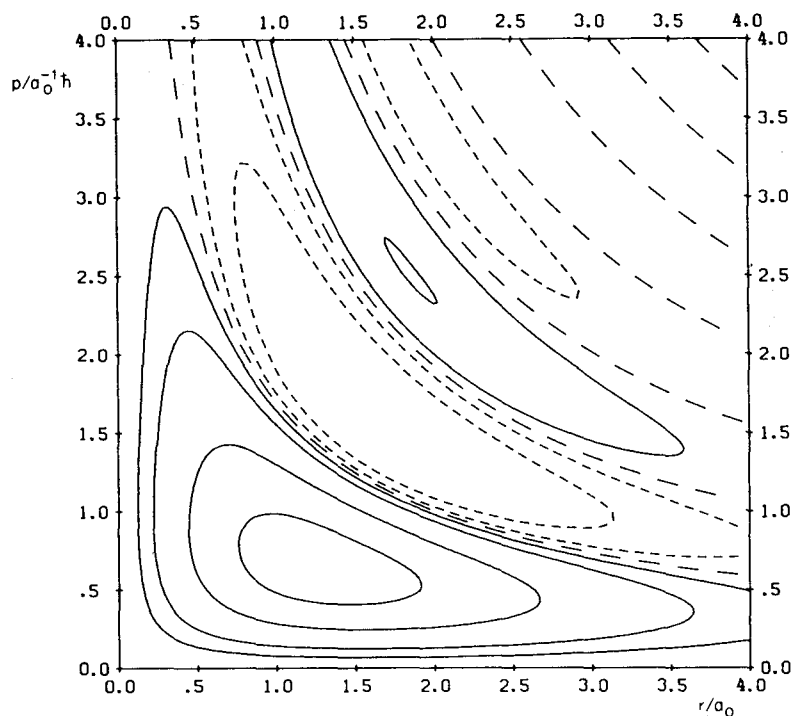


Figure 3. As figure 2 except $u = \pi/4$.

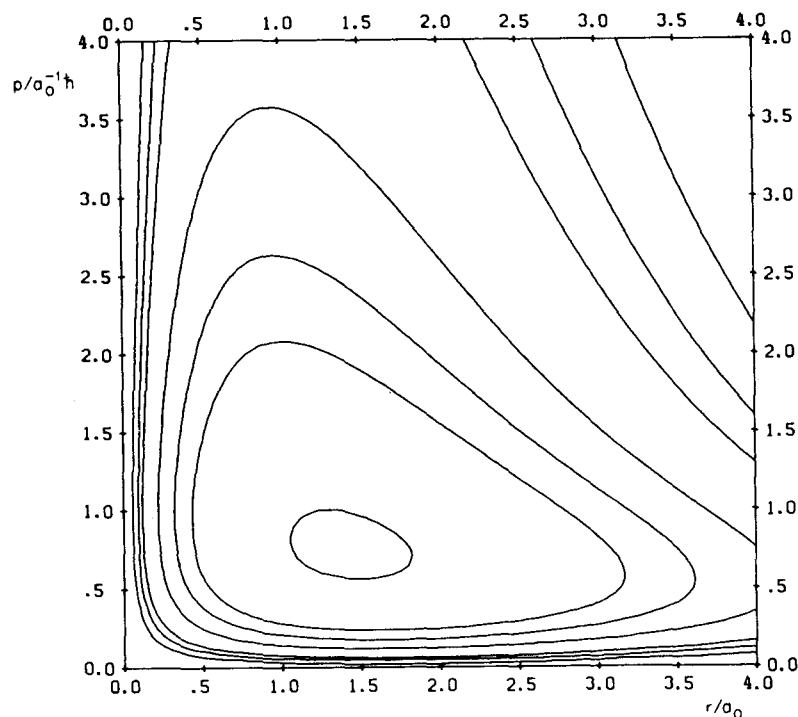


Figure 4. Contour map of the function $F_{1s}(r, p, u)$ for $u = \pi/2$. Starting from the maximum $(r_0, p_0) = (1.405 a_0, 0.759 a_0^{-1} \hbar)$, contours have been drawn at 0.3, 0.1, 0.06, 0.03, 0.01, 0.006, 0.003 \hbar^{-1} .

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This function is displayed in figures 2, 3 and 4 for u equal to 0, $\pi/4$ and $\pi/2$ respectively. For $u = \pi/2$ it is non-negative everywhere, but for all other values of u it has negative as well as positive regions.

For several purposes it is sufficient to know the function obtained from (38) by integrating over u . We shall call this function the radial phase space function and designate it $F_{1s}(r, p)$. It satisfies the normalization condition (35). From (24) it is found to be

$$F_{1s}(r, p) = \frac{16}{\pi} r^2 p^2 \sum_{i=1}^M c_i^2 \exp(-2\alpha_i r^2) \exp\left(-\frac{p^2}{2\alpha_i}\right) + \frac{32}{\pi} r^2 p^2 \sum_{i>j=1}^M c_i c_j \left(\frac{\gamma_{ij}}{\alpha_i + \alpha_j}\right)^{3/4} \times \exp(-\gamma_{ij} r^2) \exp\left(-\frac{p^2}{\alpha_i + \alpha_j}\right) j_0(2\tau_{ij} p r), \quad (39)$$

where

$$j_0(x) = \frac{\sin x}{x} \quad (40)$$

is a spherical Bessel function.

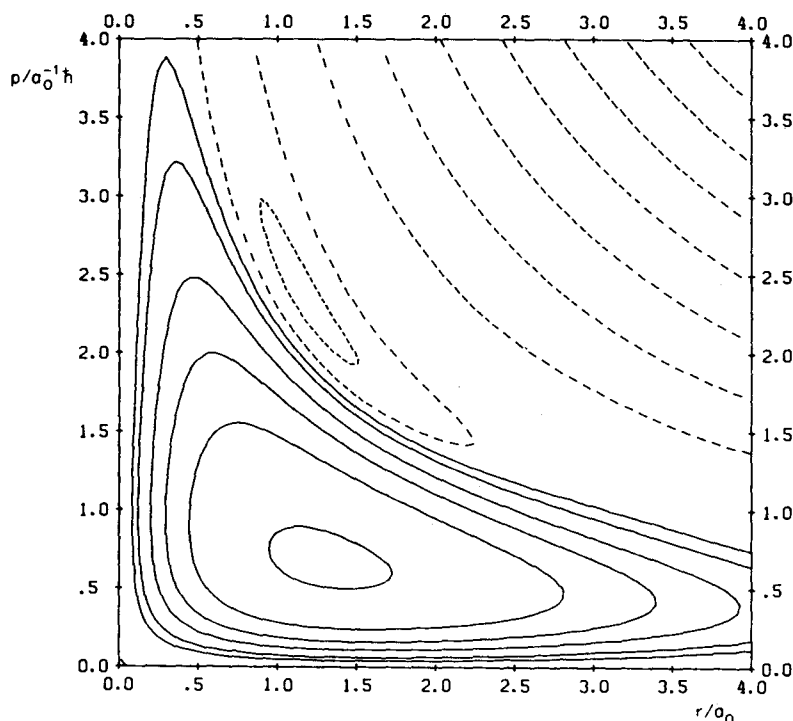


Figure 5. Contour map of the function $F_{1s}(r, p)$. The function attains its maximum value, $0.5617 \hbar^{-1}$, at the point $(r_0, p_0) = (1.30 a_0, 0.68 a_0^{-1} \hbar)$. Starting from the nodal curves (dashed lines, contour value 0.0), contours have been drawn at 0.01, 0.02, 0.05, 0.1, 0.2, 0.5 \hbar^{-1} (solid lines), $-0.01 \hbar^{-1}$ (dotted lines).

The function is dominant in this region. Table 2), but the used.

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When the parameter is disclosed by figure from the expression (39) will be crossed it is only for small α values that lead to slowly decreasing α value is much in (39) approach

Applying a series of maps for the function when both p and r are small as in figures 2 and 3. The length becomes negative everywhere.

The damped counterparts in the appearance of the Avery [26], on the

In closing this of the exact phase space question presents associated Wigner given a mathematical analysis showed that

The function $F_{1s}(r, p)$ is displayed in figure 5. It is characterized by a dominant region in which it is positive, and by an oscillatory behaviour outside this region. The amplitudes of the oscillations are, however, fairly small (see table 2), but they are definitely not due to lack of accuracy in the wavefunction used.

Table 2. Selected values of the function $F_{1s}(r, p)$ for $r=p$.

$(r/a_0) = (p/a_0^{-1} \hbar)$	$F_{1s}(r, p)/\hbar^{-1}$
0.0	0.0
0.3	0.0326
0.6	0.2676
0.9	0.4648
1.2	0.3015
1.5	0.0473
1.8	-0.0047
2.1	0.0081
2.4	-0.0031
2.7	0.0014
3.0	-0.00063
3.3	0.00021

When the product of p and r is large, a regular albeit weak damped wave is disclosed by figure 5. The presence of such a wave is readily understandable from the expression (39). When both r and p are large, the dominant terms in (39) will be cross terms for which one α is large and the other α is small, since it is only for such terms that both γ_{ij} and $1/(\alpha_i + \alpha_j)$ become small and hence lead to slowly decaying exponentials. Since (23) shows that $|\tau_{ij}| \approx 1$ when one α value is much larger than the other, we find that the relevant Bessel functions in (39) approach $j_0(pr)$, and this leads to a damped wave as observed.

Applying a similar argument to the expression (24) shows that the contour maps for the functions $F_{1s}(r, p, u)$ must disclose damped oscillations in $\cos(2\mathbf{p} \cdot \mathbf{r})$ when both p and r are large. That this is in fact the case is apparent from figures 2 and 3. In figure 4, $\cos(2\mathbf{p} \cdot \mathbf{r})$ equals 1 for all r and p (the wavelength becomes infinite), and the phase space function is accordingly non-negative everywhere.

The damped oscillations which we have discussed will, of course, have their counterparts in the theory of generalized scattering factors (cf. § 2). The appearance of the oscillations in that context has been noticed and discussed by Avery [26], on the basis of arguments quite different from ours.

In closing this section it is worthwhile drawing attention to the complexity of the exact phase space function, as compared to the simplicity of the approximate phase space function discussed in the previous section, and a natural question presents itself. What must a wavefunction look like in order that the associated Wigner function be non-negative everywhere? Hudson [27] has given a mathematical answer to this question for one-dimensional motion. His analysis showed that the wavefunction must have the form

$$\psi(x) = \exp \left[-\frac{1}{2}(ax^2 + 2bx + c) \right], \quad (41)$$

where a , b are arbitrary complex numbers with $\text{Re } a > 0$ and the complex number c is chosen so as to ensure correct normalization. When $\text{Im } a$ is zero, this wavefunction describes a minimum uncertainty state [28] in one dimension.

The conclusions of Hudson may probably be extended to three dimensions in a straightforward manner. That the wavefunction (31) describes a minimum uncertainty state in three dimensions is in accordance with this assumption.

6. THE DOMINANT SUBSPACE AND THE CLASSICAL SUBSPACE

The function $F_{1s}(r, p)$ of (39) and figure 5 was obtained from the function $F_{1s}(r, p, u)$ of (38) by integrating over u . It is interesting to integrate over r and p instead to obtain a function $F_{1s}(u)$, normalized such that

$$\int_0^\pi F_{1s}(u) \sin u \, du = 1. \quad (42)$$

The expression for this function is found to be

$$F_{1s}(u) = \frac{1}{2} \sum_{i=1}^{10} c_i^2 + \sum_{i>j=1}^{10} c_i c_j \sigma_{ij}^{3/4} (\sigma_{ij} - 2\tau_{ij}^2 \cos^2 u) / (\sigma_{ij} + \tau_{ij}^2 \cos^2 u)^{5/2} \quad (43)$$

with τ_{ij} as defined by (23) and

$$\sigma_{ij} = \frac{4\alpha_i \alpha_j}{(\alpha_i + \alpha_j)^2}. \quad (44)$$

Figure 6 shows the functions $F_{1s}(u)$ and $F_{1s}(u) \sin u$. Both functions have a sharp maximum at $u = \pi/2$.

Thus, the condition $u = \pi/2$ defines a *dominant* subspace in which the Wigner function finds its maximum support. As already seen (figure 4), the function is everywhere non-negative in this subspace.

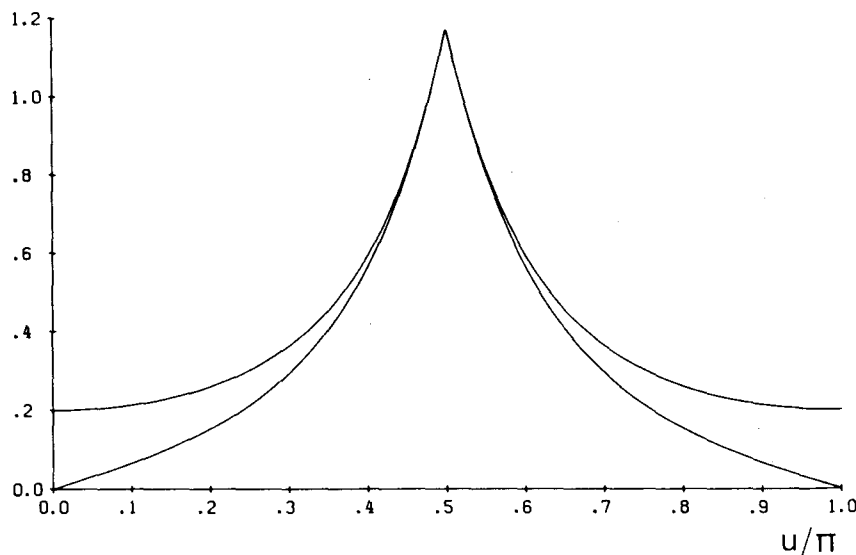


Figure 6. The functions $F_{1s}(u)$ (upper curve) and $F_{1s}(u) \sin u$ (lower curve) as a function of u/π .

The dominant subspace of and $p = 1/a_0$ subspace to mechanics, $r = 1/a_0$, in v $p = 1/\hbar a_0^{-1}$ space.

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The dominant subspace is five-dimensional. It contains a three-dimensional subspace of particular interest, namely the subspace obtained by putting $r = 1 a_0$ and $p = 1 a_0^{-1} \hbar$. It is represented by the point (1, 1) in figure 4. This is the subspace to which the ground state motion was restricted in early quantum mechanics, since a Bohr orbit (in ordinary space) was just a circle with radius $r = 1 a_0$, in which the electron was supposed to move with the constant momentum $p = 1 \hbar a_0^{-1}$. Hence we shall call the subspace in question the classical subspace.

The following important statement may now be made, on the basis of the present section and figures 2 and 3. The Wigner function attains a large, positive and constant value in the classical subspace. It is also large and positive in a large region surrounding this subspace. In particular, it is everywhere non-negative in the dominant subspace. The regions in which the Wigner function becomes negative are well separated from the classical subspace.

7. THE ANGULAR MOMENTUM DILEMMA

In this section we shall comment on the angular momentum of the 1s state, as calculated by the expression on the right hand side of (10). $a(\mathbf{r}, \mathbf{p})$ is, as mentioned in § 1, the Weyl transform of the operator \hat{a} . The Weyl correspondence is discussed in the Appendix and there it is shown that if \hat{a} is a component of the angular momentum vector operator, say

$$\hat{l}_3 = \hat{x}_1 \hat{p}_2 - \hat{x}_2 \hat{p}_1 \quad (45)$$

then $a(\mathbf{r}, \mathbf{p})$ is the same component of the classical angular momentum vector, that is,

$$l_3 = x_1 p_2 - x_2 p_1. \quad (46)$$

As is well known, the left hand side of (10) is zero when $|\psi\rangle$ is the 1s state and \hat{a} is \hat{l}_1 , \hat{l}_2 or \hat{l}_3 . Hence the right hand side must also be zero. That this is actually the case is easily seen by remembering that $f(\mathbf{r}, \mathbf{p})$ is independent of the Euler angles α , β and γ . This makes all directions of the vector \mathbf{e}_3 in (27) equivalent. But the direction of \mathbf{e}_3 is also seen to be the direction of the angular momentum vector and thus each component of this vector does in fact have a zero mean value.

As regards the length of the angular momentum vector, it is shown in the Appendix that the classical function

$$\lambda^2 = l_1^2 + l_2^2 + l_3^2 \quad (47)$$

is the Weyl transform of the operator

$$\hat{\lambda}^2 = \hat{l}_1^2 + \hat{l}_2^2 + \hat{l}_3^2 + \frac{3}{2} \hbar^2. \quad (48)$$

Evaluating the right hand side of (10) with $a(\mathbf{r}, \mathbf{p}) = \lambda^2$ will accordingly produce the value $\frac{3}{2} \hbar^2$.

This interesting result allows us to resolve a pedagogical dilemma which has bothered writers of elementary textbooks [29]. How does one bring the fact that the angular momentum in a Bohr orbit is \hbar into accordance with the fact that the angular momentum in the Schrödinger picture is zero?

The dilemma is obviously resolved by remarking that the operator that occurs in the Schrödinger picture, viz.

$$\hat{l}^2 = \hat{l}_1^2 + \hat{l}_2^2 + \hat{l}_3^2 \quad (49)$$

is different from the operator that corresponds to the classical function λ^2 of (47). Averaging λ^2 over the classical subspace described in the previous section does in fact give the value \hbar^2 , as in the Bohr description.

8. LOCAL DENSITIES

An advantage of the phase space formulation of quantum mechanics is that it leads to a natural definition of a local density in coordinate space for a given operator and a given state. Thus (10) suggests that we consider the quantity

$$\alpha(\mathbf{r}) = \int d\mathbf{p} f(\mathbf{r}, \mathbf{p}) a(\mathbf{r}, \mathbf{p}) \quad (50)$$

as being the local density associated with the operator \hat{a} and the state $|\psi\rangle$. Integration over the spatial coordinate gives the expectation value of \hat{a}

$$\langle \psi | \hat{a} | \psi \rangle = \int d\mathbf{r} \alpha(\mathbf{r}). \quad (51)$$

When $a(\mathbf{r}, \mathbf{p}) = a(\mathbf{r})$, a function of \mathbf{r} alone, we may use (8) to get

$$\alpha(\mathbf{r}) = a(\mathbf{r}) \psi(\mathbf{r})^* \psi(\mathbf{r}). \quad (52)$$

As an example, the potential energy operator

$$\hat{V} = -\frac{Z}{\hat{r}} \quad (53)$$

defines the local potential energy density

$$\epsilon_P(\mathbf{r}) = -\frac{Z}{r} \psi(\mathbf{r})^* \psi(\mathbf{r}). \quad (54)$$

For the ground state of the hydrogen atom this becomes, by observing (13),

$$\epsilon_P(\mathbf{r}) = -\frac{1}{\pi} \frac{\exp(-2r)}{r}. \quad (55)$$

As an important example of an operator that is not a function of $\hat{\mathbf{r}}$ we consider the kinetic energy operator

$$\hat{T} = \frac{\hat{p}^2}{2}. \quad (56)$$

The local kinetic energy density becomes

$$\epsilon_K(\mathbf{r}) = \int d\mathbf{p} f(\mathbf{r}, \mathbf{p}) \frac{p^2}{2}. \quad (57)$$

It may be evaluated when $f(\mathbf{r}, \mathbf{p})$ is known, but as shown by Ziff *et al.* [30] and by Cohen [31] it may also be evaluated directly from the coordinate wavefunction by using (6). The result is

$$\epsilon_K(\mathbf{r}) = \frac{1}{2} (|\nabla \psi|^2 - \frac{1}{4} \nabla^2 |\psi|^2) \quad (58)$$

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$$\epsilon_K(\mathbf{r}) = \frac{1}{2}(\frac{1}{2}|\nabla\psi|^2 - \frac{1}{4}\psi^*\nabla^2\psi - \frac{1}{4}\psi\nabla^2\psi^*). \quad (59)$$

It is seen that

$$\epsilon_K(\mathbf{r}) = \frac{1}{2}(\epsilon_{KB}(\mathbf{r}) + \epsilon_{KC}(\mathbf{r})), \quad (60)$$

where

$$\epsilon_{KB}(\mathbf{r}) = \frac{1}{2}|\nabla\psi|^2 \quad (61)$$

and

$$\epsilon_{KC}(\mathbf{r}) = -\frac{1}{4}(\psi^*\nabla^2\psi + \psi\nabla^2\psi^*). \quad (62)$$

When ψ is real, $\epsilon_{KC}(\mathbf{r})$ becomes equal to

$$\epsilon_{KA}(\mathbf{r}) = -\frac{1}{2}\psi^*\nabla^2\psi. \quad (63)$$

The expressions ϵ_{KA} , ϵ_{KB} , ϵ_{KC} and ϵ_K were all discussed by Cohen [31] (who used the designations K_A , K_B , K_C and K_D , respectively). He showed that each expression could be derived from phase space descriptions discussed earlier by him [32].

For the ground state of the hydrogen atom we obtain the following explicit expressions

$$\epsilon_{KA}(\mathbf{r}) = \epsilon_{KC}(\mathbf{r}) = \frac{1}{\pi} \left(\frac{1}{r} - \frac{1}{2} \right) \exp(-2r), \quad (64)$$

$$\epsilon_{KB}(\mathbf{r}) = \frac{1}{2\pi} \exp(-2r), \quad (65)$$

$$\epsilon_K(\mathbf{r}) = \frac{1}{2\pi r} \exp(-2r). \quad (66)$$

These will be discussed further in the following section.

With reference to Cohen's work [31, 32], we want to make the comment that, although a whole set of mathematically consistent phase space representations of quantum mechanics exists, there are compelling reasons why one should consider the Weyl-Wigner representation used in the present work as the canonical one. These reasons were discussed at length in a previous paper [11].

9. A LOCAL VIRIAL THEOREM

Let

$$E_K = \langle \psi | \hat{T} | \psi \rangle, \quad (67)$$

$$E_P = \langle \psi | \hat{V} | \psi \rangle, \quad (68)$$

$$E = \langle \psi | \hat{T} + \hat{V} | \psi \rangle \quad (69)$$

be the expectation values of the kinetic energy, the potential energy and the total energy, respectively, for a stationary state of the hydrogen atom. As for any Coulomb system we then have the well-known virial theorem

$$E_K = -\frac{1}{2}E_P \quad (70)$$

which expresses a global balance between the kinetic and potential energy. Due to the obvious relation

$$E = E_K + E_P \quad (71)$$

we may also write

$$E_K = -E. \quad (72)$$

Bader and his co-workers have shown that for a molecular system it is possible to perform a spatial partitioning of the charge distribution in such a manner that the kinetic and potential energies of the resulting fragments obey the virial theorem (see [33]). For the ground state of the hydrogen atom they also noted [33] that

$$\epsilon_{KB}(\mathbf{r}) = -E|\psi|^2, \quad (73)$$

which is a local virial theorem if the right hand side is identified as the local counterpart of the total energy.

Such an identification is, however, not quite satisfactory, since the natural definition of this local energy density would be

$$\epsilon_B(\mathbf{r}) = \epsilon_{KB}(\mathbf{r}) + \epsilon_P(\mathbf{r}) \quad (74)$$

in accordance with (71) and this quantity is different from the right hand side of (73). As a consequence $\epsilon_{KB}(\mathbf{r})$ and $\epsilon_P(\mathbf{r})$ do not satisfy a local analogue of (70).

It is, on the other hand, easily seen that if we work with $\epsilon_K(\mathbf{r})$, defined through the Weyl-Wigner correspondence, then we obtain a completely satisfactory local form of the virial theorem

$$\epsilon_K(\mathbf{r}) = -\frac{1}{2}\epsilon_P(\mathbf{r}), \quad (75)$$

$$\epsilon_K(\mathbf{r}) = -\epsilon(\mathbf{r}), \quad (76)$$

$$\epsilon(\mathbf{r}) = \epsilon_K(\mathbf{r}) + \epsilon_P(\mathbf{r}). \quad (77)$$

It must be stressed, however, that this remarkable result only holds for the ground state of a hydrogen-like atom.

In forthcoming publications we plan to study the local balance between the potential and kinetic energy for other atomic and molecular systems.

10. DISCUSSION AND CONCLUSIONS

The phase space description of a quantum mechanical system is an alternative to the description based on wavefunctions. It is from several points of view a more complicated description. From other points of view it is a richer description.

The state of a system is described by a Wigner function. In the present paper we have constructed this function for the ground state of the hydrogen atom and analysed its properties. The analysis was facilitated by the introduction of concepts like the dynamical plane and the dynamical angle, the classical subspace and the dominant subspace. The orientation of the dynamical plane is closely related to the angular momentum vector; the classical subspace is that part of phase space to which the ground state motion was confined in early quantum mechanics.

The Wigner function is found to be independent of the orientation of the dynamical plane. It attains a large, positive and constant value in the classical subspace and it remains large and positive in an extended region containing that subspace. Outside this region the Wigner function shows a rich structure

which includes of r and p . W of a series of c finds its maximum in the dominant subspace.

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which includes oscillations of a de Broglie wave-like character for large values of r and p . We have illustrated the general variation over phase space by means of a series of contour maps and a graph which shows that the Wigner function finds its maximum support in the subspace where $\mathbf{r} \cdot \mathbf{p} = 0$, the so-called dominant subspace.

A dynamical variable is represented by an operator in a description based on wavefunctions. In the phase space description it is represented by an ordinary function of \mathbf{r} and \mathbf{p} . The connection between the two representations is given by the so-called Weyl correspondence which we have described in the Appendix. In § 7 we have discussed the Weyl transformation of the angular momentum and thus resolved a pedagogical dilemma which previously obscured the comparison between early quantum mechanics and the Schrödinger description.

In §§ 8 and 9 we have shown how an integration over the momentum coordinates leads to a local configuration space description of all dynamical quantities. We have then studied the local kinetic and potential energies and shown that the virial theorem is locally satisfied for the ground state of the hydrogen atom.

In forthcoming papers we shall extend the present study by including excited states, and atoms and molecules with more than one electron.

We are very grateful to Dr. Sten Rettrup for his kind assistance at an early stage of this work. We also want to thank Dr. Helge Johansen for letting us use his density contour programs and Dr. Kurt Nielsen for interesting discussions.

APPENDIX

The Weyl correspondence

To every operator \hat{a} in spin-free Hilbert space there corresponds a phase space function $a(\mathbf{r}, \mathbf{p})$, such that (10) is valid. The relation between \hat{a} and $a(\mathbf{r}, \mathbf{p})$ is given by the so-called Weyl correspondence [1], which we prefer to write in the form [11]

$$\hat{a} = \left(\frac{2}{h}\right)^3 \int \int d\mathbf{r} d\mathbf{p} a(\mathbf{r}, \mathbf{p}) \hat{\Pi}(\mathbf{r}, \mathbf{p}), \quad (\text{A } 1)$$

where $\hat{\Pi}(\mathbf{r}, \mathbf{p})$ is the inversion operator (1). \hat{a} and $a(\mathbf{r}, \mathbf{p})$ are said to be mutual Weyl transforms.

Whenever $a(\mathbf{r}, \mathbf{p})$ is a function of \mathbf{r} or \mathbf{p} alone, then \hat{a} is the same function of the vector operator $\hat{\mathbf{r}}$ or $\hat{\mathbf{p}}$. In the general case one obtains the operator \hat{a} from the function $a(\mathbf{r}, \mathbf{p})$ by the replacement of \mathbf{r} with $\hat{\mathbf{r}}$ and \mathbf{p} with $\hat{\mathbf{p}}$, followed by a proper symmetrization of products of non-commuting operators. This symmetrization is such that, if x_i and p_i are corresponding components of \mathbf{r} and \mathbf{p} , then the operator associated with the function $x_i^n p_i^m$ is

$$\begin{aligned} \hat{a} &= \frac{1}{2^n} \sum_{r=0}^n \binom{n}{r} \hat{x}_i^r \hat{p}_i^m \hat{x}_i^{n-r} \\ &= \frac{1}{2^m} \sum_{s=0}^m \binom{m}{s} \hat{p}_i^s \hat{x}_i^n \hat{p}_i^{m-s}. \end{aligned} \quad (\text{A } 2)$$

These expressions were first derived by McCoy [34].

As an important example let us consider the classical angular momentum vector

$$\mathbf{l} = \mathbf{r} \times \mathbf{p} = (x_2 p_3 - x_3 p_2, x_3 p_1 - x_1 p_3, x_1 p_2 - x_2 p_1). \quad (\text{A } 3)$$

Direct substitution does not introduce products of non-commuting operators. The Weyl transform of l is accordingly

$$\hat{\mathbf{l}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} = (\hat{x}_2 \hat{p}_3 - \hat{x}_3 \hat{p}_2, \hat{x}_3 \hat{p}_1 - \hat{x}_1 \hat{p}_3, \hat{x}_1 \hat{p}_2 - \hat{x}_2 \hat{p}_1) \quad (\text{A } 4)$$

which is just the ordinary quantum mechanical angular momentum vector.

For the square of an angular momentum component, l_3 say, we obtain

$$l_3^2 = x_1^2 p_2^2 + x_2^2 p_1^2 - 2x_1 p_1 x_2 p_2. \quad (\text{A } 5)$$

Symmetrization according to (A 2) gives the corresponding operator which we denote $\hat{\lambda}_3^2$

$$\hat{\lambda}_3^2 = \hat{x}_1^2 \hat{p}_2^2 + \hat{x}_2^2 \hat{p}_1^2 - \frac{1}{2}(\hat{x}_1 \hat{p}_1 + \hat{p}_1 \hat{x}_1)(\hat{x}_2 \hat{p}_2 + \hat{p}_2 \hat{x}_2). \quad (\text{A } 6)$$

Squaring the third component of $\hat{\mathbf{l}}$ gives, on the other hand, the operator

$$\hat{l}_3^2 = \hat{x}_1^2 \hat{p}_2^2 + \hat{x}_2^2 \hat{p}_1^2 - \hat{x}_1 \hat{p}_1 \hat{p}_2 \hat{x}_2 - \hat{p}_1 \hat{x}_1 \hat{x}_2 \hat{p}_2. \quad (\text{A } 7)$$

Using the commutation relation

$$[\hat{x}_k, \hat{p}_k] = i\hbar \quad (\text{A } 8)$$

twice shows that

$$\hat{\lambda}_3^2 = \hat{l}_3^2 + \frac{1}{2}\hbar^2 \quad (\text{A } 9)$$

and hence that

$$\hat{\lambda}^2 = \hat{l}^2 + \frac{3}{2}\hbar^2, \quad (\text{A } 10)$$

where

$$\hat{\lambda}^2 = \hat{\lambda}_1^2 + \hat{\lambda}_2^2 + \hat{\lambda}_3^2 \quad (\text{A } 11)$$

and

$$\hat{l}^2 = \hat{l}_1^2 + \hat{l}_2^2 + \hat{l}_3^2. \quad (\text{A } 12)$$

Thus, there is a difference of $\frac{3}{2}\hbar^2$ between the Weyl transform of l^2 and the ordinary quantum mechanical operator \hat{l}^2 . This difference was apparently first noticed by Shewell [35] in connection with a general discussion of correspondence and symmetrization rules.

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